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ORGANIC POLYRADICAL MODELS FOR ORGANIC MAGNETIC MATERIALS

by David A. Modarelli, Frank C. Rossitto, Masaki Minato, and Paul M. Lahti*

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ABSTRACT

A variety of model organic high spin molecules based upon coupled phenoxy and phenylnitrene systems has been examined by semiempirical MO-CI theory. Experimental methodology using photochemical and thermal methods in solution and solid phases to generate and study phenoxy groups for investigation of these models is presented.

INTRODUCTION

Recent interest in organic polyradicals has been part of a general interest in new magnetic molecules of potential use as information storage materials. Various types of organic or organometallic magnetic materials have been recently described.[1] We have been interested primarily in materials based upon through-bond and through-space high spin coupling of many radicals (or other high spin centers such as nitrenes) to produce very high spin polyradicals.

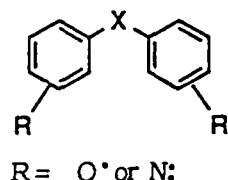
Experimental work such as Iwamura's[2] has shown that the strategy of coupling carbenes through conjugating groups -- in accordance with qualitative rules[3-5] predicting high spin coupling -- can lead to very high spin organic molecules, albeit under conditions of high dilution in crystalline or frozen solution matrix at cryogenic conditions. We wish to couple phenoxy based radicals together to form such very high spin systems. Although one gets only one spin per center -- as opposed to two per center for carbenes and nitrenes -- the greater intrinsic stability of phenoxy based systems by comparison to the more reactive high spin centers makes their synthesis attractive. Recent efforts to prepare phenoxy based polymer systems by solution oxidation of hindered phenolic systems have not yielded high spin counts,[1,6] but the reason for this failure at present is not entirely clear.

In this paper, we qualitatively summarize the application of our previously described[7-8] semiempirical computational algorithms to selected phenoxy based diradicals, and the relationship of these computations to connectivity-based models described by other workers.[3] Experimentally, we show how use of our previously developed photochemical and thermal methods[9] for solid state generation of stable phenoxyl radical centers may be extended to production of unhindered phenoxy systems under conditions where they may be readily detected and observed. *Meta* and *para*-stilbeneoxyl radicals have both been readily generated in matrix and in neat precursor matrix, studied by electron spin resonance (ESR) and ultraviolet-visible (UV-vis) spectroscopy, and their decomposition behavior in polymeric matrices elucidated. Similar experiments have been carried out for other non-*tert*-butylated phenoxy derivatives. By these and similar experiments, we hope to understand what types of phenoxy based systems are fairly robust under matrix isolation conditions (polymer matrices at room temperature and above), how efficiently our methods allow production of phenoxyl radicals under various conditions of precursor substitution and matrix type, and how plausible are the hopes of generating *and* partially orienting such radicals in polymeric matrix in an effort to control their magnetic interaction with one another. In addition, we have modified the preparation of poly(3,5-di-*tert*-butyl-4-hydroxystyrene), a known polymer[10] with the potential to be functionalized to derivatives which may be photochemically or thermally "developed" to produced high densities of radical sites while in the solid state.

COMPUTATIONAL METHODS

The semiempirical molecular orbital AM1 method in the program AMPAC[11] (version 2.10) was used in all computations. Geometries were optimized using triplet wave-functions for diradicals, with either a planar constraint or full optimization. The relative energies for triplet and singlet states of the molecules were computed using the configuration interaction

Figure 1: Molecules Investigated by AM1-CI.

	X	Connectivity ¹	Type ²
	1	(none)	m,p'
	2		m,m'
	3	-CH=CH-	m,p'
	4		m,m'
	5	-(CH=CH) ₂ -	m,p'
	6		m,m'
	7	-C≡C-	m,p'
	8		m,m'
	9	-(C≡C) ₂ -	m,p'
	10		m,m'
	11	p - phenylene	m,p'
	12		m,m'
	13	m-phenylene	m,p'
	14		m,m'
	15		p,p'
	16	=C=O	m,p'
	17		m,m'
	18		p,p'
	19	=C=CH ₂	m,p'
	20		m,m'
	21		p,p'
	22	-O-	m,p'
	23		m,m'
	24		p,p'
	25	-NH-	m,p'
	26		m,m'
	27		p,p'

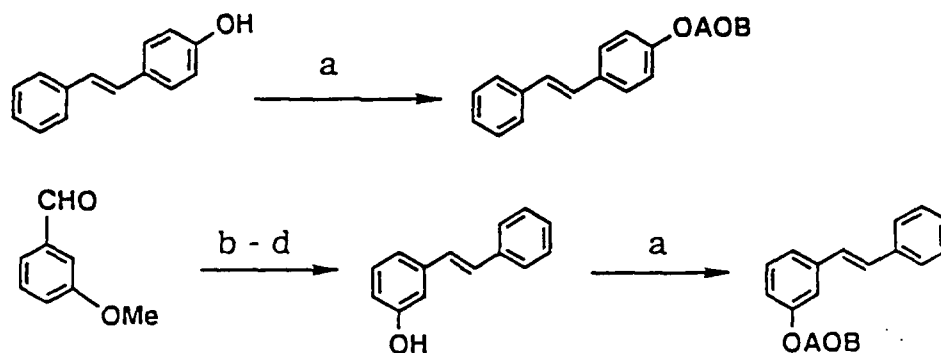
¹Connectivity of the spin system. ² Type refers to type of spin coupling, with F=ferromagnetic A=antiferromagnetic, S=strong. W=weak, * = does not follow eqn. 1. (cf. ref. 12 for 22-27)

(CI) routine in AMPAC, with six or seven orbitals used in the CI active space. Results for triplet-singlet (T-S) energy gaps were not greatly affected by modest amounts of torsion up to -30° about single bonds, in cases where planarity of the molecules was not enforced. Figure 1 summarizes the qualitative results of the computations, fuller details of which will be published elsewhere.[1,12]

EXPERIMENTAL SECTION

The synthetic routes used to prepare the stilbenoid aryloxyoxalyl *tert*-butylperoxides (AOB's) used in this study are shown schematically in Figure 2. *Para*-hydroxystilbene, phenylacetic acid, and *meta*-anisaldehyde were obtained from Aldrich Chemical Company. The general method for preparing the AOB's is described in a previous publication,[9] using the method of adding *tert*-butylperoxyoxalyl chloride to phenolic anions. NOTE THAT *tert*-butylperoxyoxalyl chloride MAY DECOMPOSE WITH POTENTIALLY HAZARDOUS VIOLENCE UNDER SOME CONDITIONS. IT SHOULD BE MADE ONLY IN SMALL (not more than two gram) QUANTITIES AND USED AS SOON AS POSSIBLE. Polymeric films were cast *in vacuo* using 10% degassed chloroform solutions of AOB precursors with polystyrene (PS, MW = 250,000) and poly-methylmethacrylate (PPMA, Aldrich medium molecular weight). Photochemical irradiations were performed with a 1000W Xenon arc lamp (Pyrex filtered for ESR). Low temperature UV-vis spectra were obtained on a Shimadzu UV-260 spectrophotometer using a special low temperature cell in an APD Cryogenics Displex circulating closed-cycle helium cryostat using Suprasil II windows; temperatures were measured by use of a gold-chromel thermocouple at the top of the cell. Low temperature ESR spectra were obtained using sealed-

Figure 2: Synthesis of Stilbene AOB Esters New to This Study.



AOB = $-(CO)-(CO)-OO^tBu$

a. BuLi/ether, then $Cl(COCO)OO^tBu$

b. $PhCH_2CO_2H$, Et_3N

c. copper chromite, quinoline, 200° , $-CO_2$

d. BBr_3

All new compounds identified by spectroscopic techniques. Adequate elemental analyses are obtained for new compounds, except for AOB esters, which tend to decompose during analysis..

in-quartz, three-fold pump-thawed samples in a Suprasil dewar at 77K (liquid nitrogen) on an IBM Instruments ESP-300 spectrometer at 9.602 GHz with computer-averaged scanning on an Aspect 3000 computer.

RESULTS AND DISCUSSION

Computational Findings

Qualitative connectivity based models have made predictions about the ground state (GS) spin multiplicity of diradicals for some time.[3-5] We exemplify these by use of a valence bond model, the Ovchinnikov criterion,[3] for which an alternant conjugated π -system with n_s starred sites and n_o unstarred sites, has multiplicity M given by equation 1. We find that this

$$M = n_s - n_o \quad (1)$$

equation gives results in accord with our computations when M is predicted to be nonzero (*i.e.*, high spin). There is less qualitative agreement when M is predicted to be zero -- a singlet GS. In accord with the Hund rule, we sometimes find a nonzero GS to be favored by a small margin even when $M = 0$. Recent experimental evidence appears to favor our computations,[13] suggesting that connectivity-based predictions of singlet GS multiplicities for diradicals should be used with caution, and checked where possible by computational methods like ours.

However, we have found equation 1 quite in agreement with our computational results for $M > 0$, even where heteroatom radicals such as our phenoxy-based systems are used. Experiment has confirmed that heteroatom-perturbed polyradicals may still exhibit high spin GS's, despite the splitting of orbitals (increased HOMO-LUMO gap) that can exist in such systems.[13] We have shown previously that our method reproduces these results.[7-8] hence it is reasonable to extrapolate our method to yet unknown systems, especially in larger model systems for which *ab initio* methods are still impractical.

Our latest results indicate that coupling of nitrenes instead of radical sites does not greatly alter the qualitative predictions of equation 1 where $M > 0$, although a factor of two in the quantitative predicted multiplicity is observed due to each nitrene center have two instead of one unpaired electron. HS-LS energy gaps for dinitrenes and diphenoxy systems of the same connectivity with the same spacer group are fairly comparable, apparently indicating that the efficacy of a spacer group in coupling two open shell sites with a given multiplicity is to some

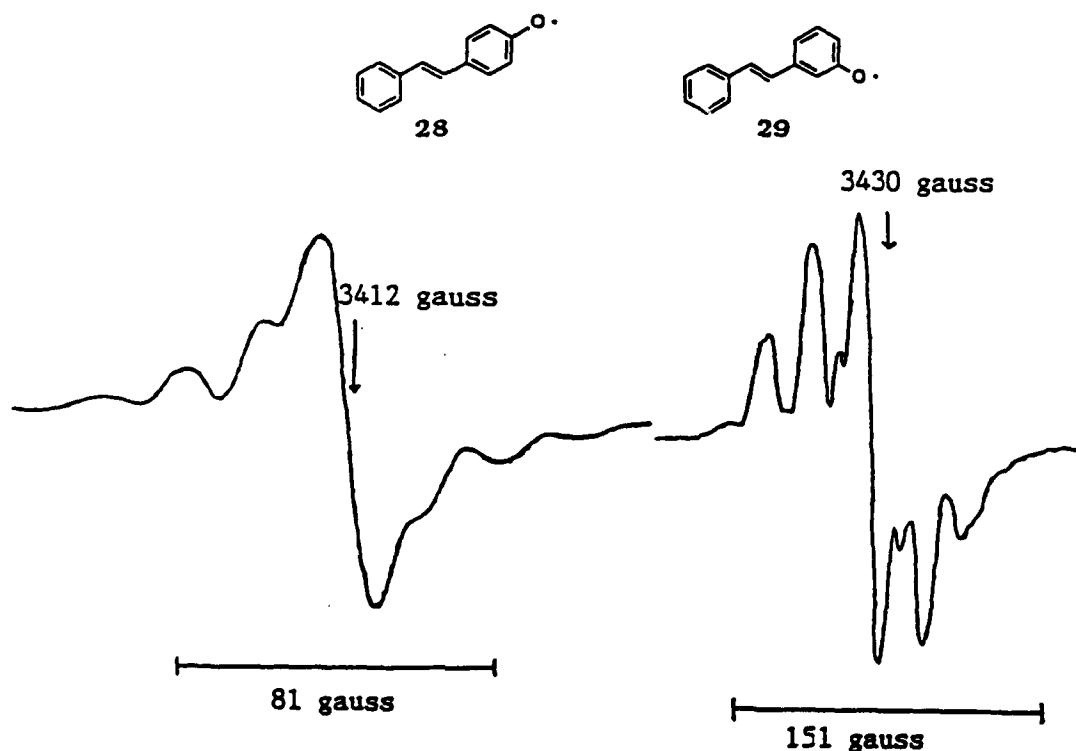
degree intrinsic to the spacer, as may be seen to some degree by the ground states shown in Figure 1. We classify the coupling as being ferromagnetic (high spin), and anti-ferromagnetic (low spin). We also note where equation 1 is not followed. For instance, the carbonyl spacer is a poor coupling spacer due to its reluctance to share the electrons in its very strong π -bond.[14] The coupling by spacers to yield high π -spin GS's are followed for both the diradical and dinitrene models. The major difference for coupled nitrenes is that the non- π unpaired electrons in dinitrenes are only weakly coupled through the σ -frameworks of the models studied, hence we often compute nearly degenerate triplet and singlet states for these systems when equation 1 gives $M = 0$ for the antiferromagnetically coupled dinitrenes.

Experimental Findings

We find that we may readily generate observable amounts of phenoxyl radical based molecules by photolysis of AOB's, both with and without radical stabilization by steric blockading. Figure 3 shows ESR spectra for **28** and **29**, generated at 77K both in 2-methyltetrahydrofuran and ethanol-pentane-ether glass. The *para* sample is deep green, the *meta* sample yellow to orange. The ESR signal and UV-vis absorbance persist until the matrix thaws. In polymeric matrix (PS or PPMA), radical generation at 77K is equally straightforward, but the ESR signal loses some resolution as expected. The lineshape of these is quite similar[10] to that noted previously in oxidation of copolymers of poly(3,5-di-*tert*-butyl-4-hydroxystyrene), **30** to the polyphenoxyl radicals. This is presumably due to the poor interaction of the radical center in the stilbeneoxyl radical with the ring that does not bear the oxy center, and is in accord with the lack of interaction computed by us in INDO computations.

In an effort to investigate the potential ability to use and preserve non-*tert*-butylated phenoxy systems in rigid polymer matrices, we took advantage of the characteristic UV-vis spectrum of **28**. In PPMA, **28** was made in the Displex at 13K, at which temperature it appears

Figure 3: ESR Spectra for Stilbeneoxy Radicals **28** and **29**.

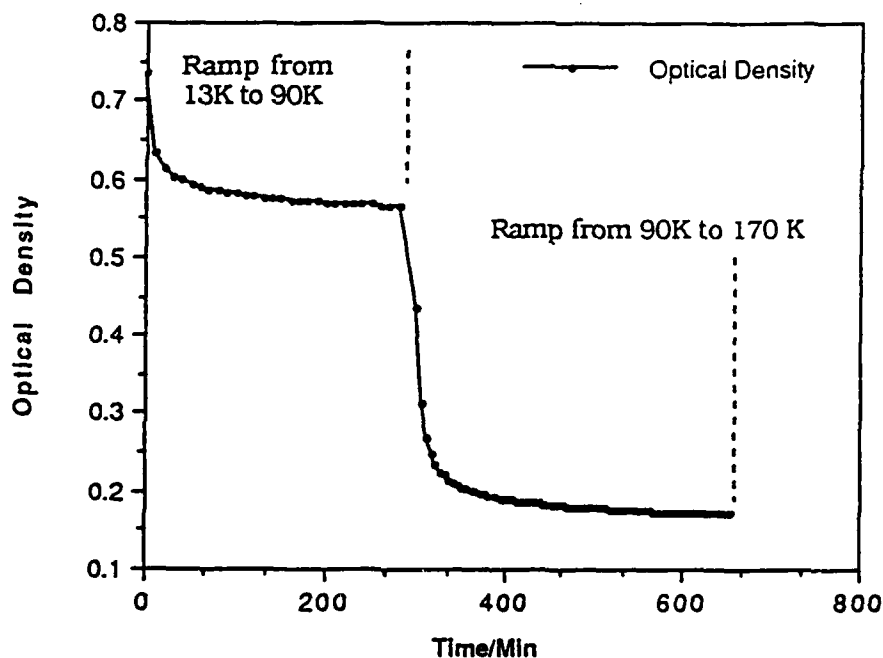


ESR spectra generated in frozen, degassed EPA glassy matrix at 77K. ESR lineshapes and widths for **28** and **29** are similar to these spectra in other frozen matrices.



to be indefinitely stable upon generation. Upon temperature ramping (maximum rate heating to various selected temperatures within 4-5 min) to 90K and 170K of this sample, the behavior of the UV-vis bands of 28 was noted as shown in Figure 4. This behavior was reproducible for different samples of 28 in PPMA and PS, as well as for 2,4,6-trichlorophenoxy similarly made. The observed sudden drop of optical density upon heating, followed by a leveling off and establishment of a constant stable concentration of radical at the new temperature, seem to us consistent with a matrix site reaction, since we are far below the softening point and glass transition temperature of the PPMA and PS matrices. We are still investigating this chemistry, but feel it plausible that at each temperature, a certain number of the leaving group *tert*-butoxyl radicals become able to attack the phenoxyl radicals by diffusion enabled through temperature rise. By the time room temperature is reached, all of the non-*tert*-butylated phenoxyl radical systems we tried were quenched by this putative process -- these included phenoxy, *meta* and *para*-stilbeneoxy, and 2,4,6-trichlorophenoxy.

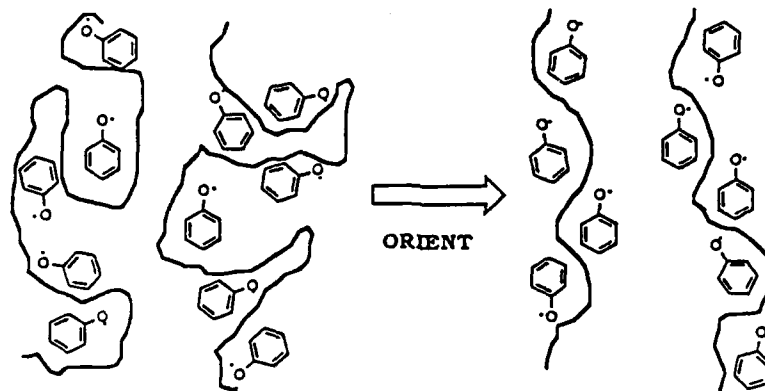
Figure 4: Thermal Decomposition of Para-Stilbeneoxy



However, sterically stabilized phenoxyl radicals, upon generation by AOB photolysis in PPMA or PS, proved to be quite stable at room temperature. Apparently, blocking of the reactive ortho positions with nonlabile *tert*-butyl groups allows these radicals to remain stable under these conditions, such that they may be observed by ESR or UV-vis spectroscopy. For instance, the color of 2,4,6-tri-*tert*-butylphenoxy -- photochemically generated in PPMA matrix -- persists at room temperature for many days under vacuum. In addition, the blocked radicals have substantial thermal stability, and may in solution remain fairly stable for at least 8 h at 70-80°C, under which conditions the precursor AOB's are completely decomposed within 3 h. We are at present further investigating the thermal stability of such systems in polymer matrices, and will report on this in due course.

We are also interested in generating phenoxyl radicals that are directly attached to polymer backbones, without necessarily being in conjugative through-bond spin interaction. Although conjugated polyradicals should give stronger spin-spin interactions and better

magnetic properties, we desired to investigate the degree to which fairly random assemblages of radicals attached to a polymer backbone may be oriented by stretching the polymer. In



principle, this can lead to through space spin-spin coupling between the radical sites, with improved magnetic properties. We have devised a simpler synthesis for the previously known 3,5-di-*tert*-butyl-4-hydroxystyrene **30**, [10,15] based upon simple reaction of two equivalents of the lithium ylid from methyltriphenylphosphonium bromide with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde in ether. Polymerization of **30** occurs under conditions similar to those used in the literature, [10] and is confirmed by ¹H NMR and IR spectroscopy. The ESR of **30** and copolymers after solution phase oxidation is also known, [10] and will not be further described here. [10] In future work we intend to make this polymer with AOB groups attached, either through polymerizing the AOB functionalized monomer, or functionalizing after polymerization. If these can be made, photochemical or thermal generation of fairly high numbers of radical centers in the solid polymeric state-- as well as study of their magnetic properties -- may become as practical as typical solution phase phenoxyl radical generation.

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